

FORM PTO-1390 (Modified)  
(REV 10-95)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

0057-2521-0 PCT

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/381295

INTERNATIONAL APPLICATION NO.  
PCT/JP98/00248INTERNATIONAL FILING DATE  
JANUARY 22, 1998PRIORITY DATE CLAIMED  
NONE

TITLE OF INVENTION

BATTERY

APPLICANT(S) FOR DO/EO/US

Shigeru AIHARA, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

## Items 13 to 18 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.  
A **SECOND** or **SUBSEQUENT** preliminary amendment.
16. ☐ A substitute specification.
17. ☐ A change of power of attorney and/or address letter.
18. ☐ Certificate of Mailing by Express Mail
19. ☒ Other items or information:

Request for Consideration of Documents Cited in International Search Report  
Drawings - Informal ( 7 Sheets )

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/381295

INTERNATIONAL APPLICATION NO.  
PCT/JP98/00248ATTORNEY'S DOCKET NUMBER  
0057-2521-0 PCT

20. The following fees are submitted.:

CALCULATIONS PTO USE ONLY

**BASIC NATIONAL FEE ( 37 CFR 1.492 (a) (1) - (5) ) :**

- ☒ Search Report has been prepared by the EPO or JPO ..... **\$840.00**
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) ..... **\$670.00**
- ☐ No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) ..... **\$760.00**
- ☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... **\$970.00**
- ☐ International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) ..... **\$96.00**

**ENTER APPROPRIATE BASIC FEE AMOUNT =****\$840.00**Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).**\$0.00**

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	13 - 20 =	0	x \$18.00
Independent claims	1 - 3 =	0	x \$78.00

**\$0.00****\$0.00**Multiple Dependent Claims (check if applicable). ☐**\$0.00****TOTAL OF ABOVE CALCULATIONS =****\$840.00**Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). ☐**\$0.00****SUBTOTAL =****\$840.00**Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).**\$0.00****TOTAL NATIONAL FEE =****\$840.00**Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). ☐**\$0.00****TOTAL FEES ENCLOSED =****\$840.00**

Amount to be:	\$
refunded	
charged	\$

☒ A check in the amount of **\$840.00** to cover the above fees is enclosed.

☐ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \_\_\_\_\_ to cover the above fees.  
A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **15-0030** A duplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO:

**OBLON, SPIVAK, McCLELLAND, MAIER & NEUSTADT, P.C.**  
Crystal Square Five, Fourth Floor  
1755 Jefferson Davis Highway  
Arlington, Virginia 22202  
703-413-3000

**WILLIAM E. BEAUMONT**  
REGISTRATION NUMBER 30,996

SIGNATURE

Norman F. Oblon

NAME

24,618

REGISTRATION NUMBER

DATE

September 22, 1998

420 Rec'd PCT/PTO 22 SEP 1999

## Description

BATTERYTechnical Field

This invention relates to a battery and, more particularly, to a battery structure that realizes a light, compact and thin battery having a high discharging capacity at a high current density and satisfactory cycle characteristics.

Background of the Invention

Batteries have been used long as a main power source or a backup power source for a variety of equipment. The demand for batteries has recently been increasing with the development of portable electronic equipment, such as cellular phones and portable personal computers. Primary batteries and secondary batteries are available according to use. As to secondary batteries having great convenience, high performance batteries such as lithium ion secondary batteries and nickel-hydrogen batteries have been attracting attention. The present invention will hereinafter be explained by referring to lithium ion secondary batteries the demand of which has been steeply increasing for use in portable electronic equipment.

Conventional lithium ion secondary batteries comprise a battery body that is a cylindrical roll of an electrode body or a stack of rectangular electrode bodies, the electrode body being

composed of a positive electrode, a negative electrode, and a separator that is interposed between the two electrodes to serve for insulation and retention of an electrolyte. The battery body is put in a metal-made case so that the positive electrode, the negative electrode and the separator can be brought into intimate contact by the pressure of the case thereby to maintain the contact between each electrode and the separator.

An electrical contact can be maintained by putting the battery body in a metal-made case, but there is a problem that the case, being made of metal, increases the weight of the battery.

Moreover, it is difficult to make a thin metal case. Difficulty in making a thin case has been a great obstacle to fulfillment of the demand for batteries to be used in compact portable equipment.

In this connection, U.S. Patent 5,437,692 discloses a structure in which a lithium ion-conducting polymer is used as an ion conducting layer, and a positive electrode and a negative electrode are joined to the ion-conducting layer with an adhesive layer containing a lithium compound. The inventors of the present invention previously proposed in Japanese Patent Application No. 8-338240 a battery structure requiring no metal-made rigid case and a process for producing the same, in which a positive electrode and a negative electrode are previously joined to a separator with an adhesive resin.

The method comprising joining a positive and a negative electrode to a lithium ion-conducting polymer with an adhesive

layer containing a lithium compound is disadvantageous in that the adhesive layer attains weak adhesion and becomes considerable resistance to ion conduction. The method comprising previously joining a positive and a negative electrode to a separator with an adhesive resin has made it feasible to maintain an electrical contact among them without imposing an external force but involves a problem that resistance between electrodes (i.e., a positive electrode and a negative electrode) increases because of the existence of not only the separator but the adhesive resin between the electrodes.

Direct bonding of electrodes is a conceivable method. In this case, it is necessary to secure both ion conduction and electron insulation between electrodes that ought to be undertaken by a conventional ion-conducting polymer or separator, and yet to join the electrodes firmly.

Further, the conventional ion-conducting polymer has weak adhesive strength, and the conventional adhesive resin joining electrodes and a separator has high adhesive strength but tends to deteriorate ion conductivity.

Where the conventional adhesive resin is used, it turned out that cases are met with in which a solution of the adhesive resin is absorbed by a porous electrode only to exhibit low adhesive strength or even fail to bond.

In addition, electrodes have their surfaces smoothed by pressing but still have unevenness of several microns to form

vacancies where a separator and the electrodes are not in contact.

The vacancies that should have been filled with an electrolyte may get starved of the electrolyte, which depends on the amount of the electrolyte supplied and the condition of use of the battery.

Starvation of the electrolyte leads to an increase of internal resistivity of the battery and reductions in battery characteristics.

The present invention has been reached, aiming at settlement of the above-described problems. It is an object of the invention to provide a light, compact and thin battery in which a positive and a negative electrode are joined firmly to maintain the adhesive strength while securing both electron insulation and ion conduction between electrodes and decreasing resistance between electrodes, i.e., internal resistance of a battery, to improve battery characteristics.

#### Disclosure of the Invention

A first battery according to the invention comprises a battery body having a positive and a negative electrode containing an active material, an electrolytic solution containing an electrolyte, and an adhesive resin layer which is interposed in between the positive electrode and the negative electrode and is joined to at least one of the positive and the negative electrodes, wherein the adhesive resin layer comprises at least one layer and contains fillers. In this structure, at least one of the positive

electrode and the negative electrode is directly bonded to the adhesive resin layer, and the filler added makes the adhesive resin layer porous. The electrolyte and an adhesive resin solution can be held in the pores. As a result, internal resistivity of the battery can be reduced while maintaining adhesive strength to provide satisfactory battery characteristics.

A second battery according to the invention is the above-described first battery, wherein the electrolyte is an organic electrolyte containing lithium ions. This mode, when applied to lithium ion secondary batteries which are required to have reduced weight and thickness, provides a high performance compact battery.

A third battery according to the invention is the above-described first battery, wherein the average particle size of the filler is equal to or smaller than the particle size of the active material of the positive and negative electrodes. According to this mode, when the positive electrode and the negative electrode are joined with an adhesive resin, an adhesive resin solution having the adhesive resin dissolved in a solvent is hardly absorbed by the electrode active material so that it can be held as an adhesive resin layer to give necessary adhesive strength.

A fourth battery according to the invention is the above-described first battery, wherein the average particle size of the filler is 1  $\mu\text{m}$  or smaller. According to this embodiment, the filler manifests a proper thickening effect for the adhesive

resin solution to make the adhesive resin solution hardly absorbable by the active material thereby securing necessary adhesive strength. Further, the filler makes the adhesive resin layer porous to improve ion conductivity thereby providing satisfactory battery characteristics.

A fifth battery according to the invention is the above-described first battery, wherein the sum of a volume ratio of the adhesive resin and that of the filler per unit volume of the adhesive resin layer is less than 1. This mode secures the porosity of the formed adhesive resin layer thereby securing satisfactory ion conduction.

A sixth battery according to the invention is the above-described first battery, wherein the sum of a volume ratio of the adhesive resin and that of the filler per unit volume of the adhesive resin layer is 0.2 to 0.8. According to this embodiment, the voids of the porous adhesive resin are filled with the electrolyte to exhibit sufficient ion conductivity.

A seventh battery according to the invention is the above-described first battery, wherein the filler comprises at least one of non-conductive materials and semiconductors. According to this mode, the adhesive resin layer can be made porous to provide excellent battery characteristics including satisfactory ion conductivity while retaining adhesive strength.

An eighth battery according to the invention is the above-described first battery, wherein the adhesive resin layer



comprises a layer containing an electrically conductive filler and a layer containing at least one of non-conductive fillers and semiconductive fillers. According to this embodiment, internal resistivity of the battery can further be diminished by the conductive filler-containing layer.

A ninth battery according to the invention is the above-described first battery, wherein the adhesive resin layer is constituted so as to fill the unevenness on the positive and the negative electrodes. This structure is effective in increasing the adhesive strength and preventing reduction of battery characteristics due to starvation of the electrolyte.

A tenth battery according to the invention is the above-described first battery, wherein the battery body is a laminate of a plurality of electrode bodies each composed of a single layer of the positive electrode, a single layer of the adhesive resin layer, and a single layer of the negative electrode.

An eleventh battery according to the invention is the above-described tenth battery, wherein the laminate is composed of the positive electrodes and the negative electrodes which are alternately interposed among a plurality of the adhesive resin layers.

A twelfth battery according to the invention is the above-described tenth battery, wherein the laminate is composed of the positive electrode and the negative electrode which are alternately interposed between adhesive resin layers and rolled

up.

A thirteenth battery according to the invention is the above-described tenth battery, wherein the laminate is composed of the positive electrode and the negative electrode which are alternately interposed between adhesive resin layers and folded.

#### Brief Description of Drawings

Fig. 1 is a diagram showing the volume ratio in the adhesive resin layer of the battery according to the invention.

Fig. 2 is a schematic cross-sectional view showing the space formed in the interface between a positive electrode and a negative electrode in the battery according to the invention.

Fig. 3 is a graph showing the change in discharge capacity brought about by addition of an alumina filler to a PVDF resin.

Fig. 4 is a graph showing the change in discharge capacity caused by addition of an alumina filler to a PVA resin.

Fig. 5 is a graph showing the relationship between peel strength and discharge capacity with an alumina filler added having a varied average particle size.

Fig. 6 is a graph showing the relationship between peel strength and discharge capacity against volume percentage of the voids of an adhesive resin layer.

Fig. 7 is a graph showing the relationship between peel strength and discharge capacity against thickness of an adhesive resin layer.

### The Best Mode for Carrying out the Invention

The modes for carrying out the invention are hereinafter described by referring to the drawings.

The present invention consists in joining a positive electrode and a negative electrode directly with an adhesive resin layer so as to reduce internal resistivity of the battery. The positive and the negative electrodes are made up of fine particles of the respective active materials bound by a binder and molded and are porous. Where an adhesive resin is used to join the positive and the negative electrodes, ion conductivity is lessened to deteriorate battery characteristics according as the amount of the adhesive resin is increased for strengthening the adhesion.

This is because the adhesive resin layer is formed in a film to block the passages for ion migration. Therefore, the problem ought to be solved only if the adhesive resin is not filmy but porous.

In the present invention the adhesive resin layer can be made porous by incorporating a filler into the adhesive resin.

If an adhesive resin solution containing no filler is applied to an electrode (a positive and a negative electrode) for bonding, the adhesive resin solution will be absorbed by the electrode that is porous. Where a filler is mixed into the adhesive resin solution, the adhesive resin layer is provided with a porous structure formed by the filler. Since the adhesive resin solution is held in the pores of the porous structure and thereby prevented

from being absorbed by the electrode, the adhesive resin solution can be maintained on the adherend surface. Further, this effect brings about an increase in viscosity of the adhesive resin solution to further improve adhesive resin holding properties.

The average particle size of the filler to be added is preferably not greater than that of the electrode active material, particularly 1  $\mu\text{m}$  or smaller. Filler particles having an average particle size of 1  $\mu\text{m}$  or greater form pores the diameter of which approximates the pore size of the electrode, and the ability of holding the electrolytic solution decreases. Where filler particles have an average particle size equal to or greater than the particle size of the electrode active material, the pores lose the ability of holding the electrolyte, resulting in reductions of battery characteristics. That is, the filler added produces no substantial effect. The sedimentation velocity of the filler particles in the adhesive resin solution increases with an increasing average particle size, which considerably deteriorates the handling properties of the adhesive resin solution. With the average particle size being 1  $\mu\text{m}$  or smaller, the filler moderately increases the viscosity of the adhesive resin solution and makes the adhesive resin layer porous. The adhesive resin solution and the electrolytic solution can thus be held in the interface between electrodes.

The preference for the above-specified particle size of the filler applies to the particles constituting the most part of

the filler. It does not matter if the filler contains particles out of that range.

An adhesive resin solution using a solution type adhesive resin is made up of a filler, an adhesive resin, and a solvent.

Since the solvent is removed on drying, the resulting adhesive resin layer is composed of the filler, the adhesive resin, and the voids formed on solvent's drying. The constitution of the adhesive resin layer is illustrated in Fig. 1. As can be seen from Fig. 1, the void volume formed by the filler is made up of the volume of the adhesive resin and the volume of the voids formed on solvent's drying. If all the void volume formed by the filler is filled with the adhesive resin, the adhesive resin layer fails to retain its porosity and becomes an insulating layer. Hence, the sum of a volume ratio of the adhesive resin and that of the filler per unit volume of the adhesive resin layer should be less than 1.

In order for the adhesive resin layer to retain porosity, it is required as stated above that the sum of a volume ratio of the adhesive resin and that of the filler per unit volume of the adhesive resin layer be less than 1. On the other hand, in order for the voids of the porous adhesive resin to be filled with an electrolytic solution to exhibit sufficient ion conductivity, it is desirable for the adhesive resin layer to have a void volume of about 30%. From this standpoint, the sum of a volume ratio of the adhesive resin and that of the filler per unit volume of the adhesive resin layer should be 0.2 to 0.8. In other words the

volume percentage of the voids based on the adhesive resin layer should be 20% to 80%.

The filler is not particularly limited in material as far as the above-specified average particle size can be realized.

Inorganic substances such as oxides, e.g.,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ , and  $\text{LiAlO}_2$ , carbides, e.g.,  $\text{SiC}$ ,  $\text{B}_4\text{C}$ , and  $\text{ZrC}$ , and nitrides, e.g.,  $\text{SiN}$ ,  $\text{BN}$ , and  $\text{TiN}$ , are stable in an electrolyte and, because they have low conductivity, there is no fear of a short circuit even where the filler-containing adhesive resin is present to connect the electrodes. Because polymers such as polyolefin resins and polymethyl methacrylate have not only low conductivity but a small specific gravity, they are effective in minimizing an increase of weight as compared with inorganic fillers or metallic fillers.

An inorganic salt, such as  $\text{LiPF}_6$  or  $\text{LiClO}_4$ , that does not dissolve in an electrolytic solution or remains undissolved can serve as a filler to form fine pores. Even where the inorganic salt dissolves in an electrolytic solution, it leaves pores in the adhesive resin layer after dissolving, making it possible to increase the porosity of the adhesive resin layer.

Where a conductive filler, such as carbon or metal, is used, the adhesive resin layer is endowed with electrical conductivity.

The adhesive resin layer thus having conductivity, electron conduction is not hindered even if the adhesive resin enters the interstices of an electrode. However, in case such a conductive material as carbon is used, the adhesive resin layer loses the

function of insulation, requiring some manipulation for prevention of a short circuit between the electrodes. A short circuit can be prevented by, for example, joining the electrodes via a three-layered adhesive resin layer composed of a pair of adhesive resin layers containing a conductive filler and an adhesive resin layer containing an insulating filler interposed therebetween. A short circuit can also be prevented by joining the electrodes via a two-layered adhesive resin layer composed of a layer containing a conductive filler and a layer containing an insulating filler.

It is primarily required of the adhesive resin layer to have insulating properties against electron conduction between each electrode. In addition, where the filler-containing adhesive resin layer has such a form as to fill the space existing on the surface of each electrode due to the surface unevenness, the adhesive strength increases, and reduction in battery characteristics due to shortage of the electrolyte can be prevented.

Because the surface of an electrode has not a little unevenness on the order of several microns, it is desirable that the filler-containing adhesive resin be present so as to fill the gap as shown in Fig. 2. Supposing an allowable reduction in discharge capacity due to resistance of the adhesive resin layer is up to 50%, a desirable thickness of the adhesive resin layer is 200  $\mu\text{m}$  or smaller. In order to minimize the reduction in discharge capacity, a more desirable thickness of the adhesive resin layer is 50  $\mu\text{m}$  or smaller.

While the shape of the filler to be added to the adhesive resin is not particularly limited, it includes a spherical shape, an elliptical shape, a fibrous shape, and a flaky shape. A spherical filler will achieve an increased packing density, making the adhesive resin layer thinner. An elliptical, fibrous or flaky filler has an increased specific surface area to increase the void volume of the adhesive resin layer.

While the adhesive resin is not particularly limited in kind, materials which, when present in battery materials, are not corroded by an electrolytic solution containing an electrolyte or an electrode-forming material and are capable of retaining adhesiveness are preferred. In particular, adhesive resins of solution type are more effective, for the adhesive resin layer can easily be made porous. In lithium ion secondary batteries containing an organic electrolyte, fluorocarbon resins represented by polyvinylidene fluoride (PVDF) and polymers containing polyvinyl alcohol in the molecular structure thereof, represented by polyvinyl alcohol, are preferred.

While not limiting, the adhesive resin is preferably applied in a manner agreeable with a desired thickness and a coating form. Illustrative examples of coating methods include screen printing, bar coating, roll coating, gravure printing, and doctor blade coating.

The invention does not impose particular restriction on the structure of batteries to which the invention is applied. The



invention is applicable to batteries having a battery body comprising a positive electrode, a negative electrode, and an adhesive resin layer interposed between the electrodes. Accordingly, the battery body can be an electrode body composed of a single positive electrode layer, a single adhesive resin layer, and a single negative electrode layer (hereinafter referred to as a unit electrode body) or a laminated battery body comprising a plurality of such unit electrode bodies. When the invention is applied to a battery having such a laminated battery body, there is provided a battery having high performance and a high battery capacity.

The laminated battery body can be formed by alternately superposing a plurality of positive electrodes and negative electrodes all cut in sizes via an adhesive resin layer or by rolling or folding one or more than one continuous sets of a positive electrode and a negative electrode to form a structure in which the positive electrode and the negative electrode alternate via an adhesive resin layer.

The present invention is especially effective when applied to lithium secondary batteries, which is not limiting the application of the invention. The invention is also applicable to primary batteries, such as lithium primary batteries, manganese-zinc batteries, and silver-zinc batteries; and other types of secondary batteries, such as nickel-cadmium batteries, nickel-zinc batteries, nickel-hydrogen batteries, polymer

batteries, and carbon secondary batteries.

The details of the invention will now hereinafter be given by way of Examples, but the invention is by no means limited thereto.

#### EXAMPLE 1

Preparation of electrode body:

A positive electrode active material layer consisting of 91 parts by weight of  $\text{LiCoO}_2$  having an average particle size of 10  $\mu\text{m}$  (produced by Nippon Chemical Industrial Co., Ltd.), 6 parts by weight of graphite powder (produced by LONZA Ltd.), and 3 parts by weight of polyvinylidene fluoride (produced by Kureha Chemical Industry Co., Ltd.) was applied to an aluminum foil substrate to an average coating thickness of 80  $\mu\text{m}$  to form a positive electrode.

A negative electrode active material layer consisting of 90 parts by weight of mesophase microbeads (produced by Osaka Gas Co., Ltd.) having an average particle size of 8  $\mu\text{m}$  and 10 parts by weight of polyvinylidene fluoride was applied to a copper substrate to an average coating thickness of 80  $\mu\text{m}$  to form a negative electrode.

An adhesive resin solution for joining these electrodes was prepared by dispersing and dissolving polyvinylidene fluoride (produced by Elf Atochem Japan) and alumina powder having an average particle size of 0.01  $\mu\text{m}$  (produced by Degussa Corporation) in a concentration of 10 wt% each in N-methylpyrrolidone. The positive electrode and the negative electrode were cut in sizes of 50 mm x 50 mm and 55 mm x 55 mm, respectively. A cut piece of the negative electrode was coated with the adhesive resin solution on



Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving 2 wt% of polyvinyl alcohol and 5 wt% of alumina powder having an average particle size of 0.01  $\mu\text{m}$  in N-methylpyrrolidone.

#### COMPARATIVE EXAMPLE 2

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 2, except for using an adhesive resin solution prepared by dissolving 2 wt% of polyvinyl alcohol in N-methylpyrrolidone.

#### EXAMPLE 3

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 10 wt% of alumina powder having an average particle size of 0.1  $\mu\text{m}$  in N-methylpyrrolidone.

#### EXAMPLE 4

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 10 wt% of alumina powder having an average particle size of 1  $\mu\text{m}$  in N-methylpyrrolidone.

#### EXAMPLE 5

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 10 wt% of silica powder having an average particle size of 0.007  $\mu\text{m}$  in N-methylpyrrolidone.

#### COMPARATIVE EXAMPLE 3

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 10 wt% of alumina powder having an average particle size of 10  $\mu\text{m}$  in N-methylpyrrolidone.

#### EXAMPLE 6

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 5 wt% of alumina powder having an average particle size of 0.01  $\mu\text{m}$  in N-methylpyrrolidone.

#### EXAMPLE 7

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 5 wt% of polyvinylidene fluoride and 25 wt% of alumina

powder having an average particle size of 0.01  $\mu\text{m}$  in N-methylpyrrolidone.

#### COMPARATIVE EXAMPLE 4

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 1 wt% of alumina powder having an average particle size of 0.01  $\mu\text{m}$  in N-methylpyrrolidone.

#### COMPARATIVE EXAMPLE 5

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 3 wt% of polyvinylidene fluoride and 30 wt% of alumina powder having an average particle size of 0.01  $\mu\text{m}$  in N-methylpyrrolidone.

#### EXAMPLE 8

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 10 wt% of alumina powder having an average particle size of 0.01  $\mu\text{m}$  in N-methylpyrrolidone and using a 150 mesh screen for applying the adhesive resin solution (the thickness of the resulting adhesive resin layer was 50  $\mu\text{m}$ ).

#### EXAMPLE 9

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 10 wt% of alumina powder having an average particle size of 0.01  $\mu\text{m}$  in N-methylpyrrolidone and using a 100 mesh screen for applying the adhesive resin solution (the thickness of the resulting adhesive resin layer was 100  $\mu\text{m}$ ).

#### EXAMPLE 10

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 10 wt% of alumina powder having an average particle size of 0.01  $\mu\text{m}$  in N-methylpyrrolidone and using a 60 mesh screen for applying the adhesive resin solution (the thickness of the resulting adhesive resin layer was 150  $\mu\text{m}$ ).

#### EXAMPLE 11

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 10 wt% of alumina powder having an average particle size of 0.01  $\mu\text{m}$  in N-methylpyrrolidone and using a 250 mesh screen for applying the

adhesive resin solution (the thickness of the resulting adhesive resin layer was 10  $\mu\text{m}$ ).

#### EXAMPLE 12

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 10 wt% of alumina powder having an average particle size of 0.01  $\mu\text{m}$  in N-methylpyrrolidone and using a 50 mesh screen for applying the adhesive resin solution (the thickness of the resulting adhesive resin layer was 200  $\mu\text{m}$ ).

#### EXAMPLE 13

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 10 wt% of silica powder having an average particle size of 0.01  $\mu\text{m}$  (produced by Aerosil Co., Ltd.) in N-methylpyrrolidone.

#### EXAMPLE 14

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 30 wt% of silicon carbide powder having an average particle size of 0.5  $\mu\text{m}$  (produced by Seimi Chemical Co., Ltd.) in N-methylpyrrolidone and using a



100 mesh screen in applying the adhesive resin solution.

#### EXAMPLE 15

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 30 wt% of boron carbide powder having an average particle size of 0.5  $\mu\text{m}$  (produced by Seimi Chemical Co., Ltd.) in N-methylpyrrolidone.

#### EXAMPLE 16

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 30 wt% of silicon nitride powder having an average particle size of 0.5  $\mu\text{m}$  (produced by Seimi Chemical Co., Ltd.) in N-methylpyrrolidone.

#### EXAMPLE 17

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 5 wt% of polymethyl methacrylate (PMMA) powder having an average particle size of 0.5  $\mu\text{m}$  in N-methylpyrrolidone.

#### EXAMPLE 18

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for

using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride, 9 wt% of alumina powder having an average particle size of 0.01  $\mu\text{m}$ , and 1 wt% of alumina powder having an average particle size of 1  $\mu\text{m}$  in N-methylpyrrolidone.

#### EXAMPLE 19

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride, 5 wt% of alumina powder having an average particle size of 0.01  $\mu\text{m}$ , and 5 wt% of silica powder having an average particle size of 0.01  $\mu\text{m}$  in N-methylpyrrolidone.

#### EXAMPLE 20

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride, 9 wt% of alumina powder having an average particle size of 0.01  $\mu\text{m}$ , and 9 wt% of silica powder having an average particle size of 0.5  $\mu\text{m}$  in N-methylpyrrolidone.

#### EXAMPLE 21

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and

dispersing 10 wt% of polyvinylidene fluoride, 9 wt% of alumina powder having an average particle size of 0.01  $\mu\text{m}$ , and 1 wt% of polymethyl methacrylate powder having an average particle size of 0.5  $\mu\text{m}$  in N-methylpyrrolidone.

#### EXAMPLE 22

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride, 9 wt% of alumina powder having an average particle size of 0.01  $\mu\text{m}$ , and 1 wt% of alumina powder having an average particle size of 0.5  $\mu\text{m}$  in N-methylpyrrolidone.

#### EXAMPLE 23

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1, except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride, 5 wt% of silicon carbide powder having an average particle size of 0.5  $\mu\text{m}$ , and 5 wt% of polymethyl methacrylate powder having an average particle size of 0.5  $\mu\text{m}$  in N-methylpyrrolidone.

#### EXAMPLE 24

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1 except for the following. An adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 20 wt% of iron

652260 5521860

powder having an average particle size of  $0.5\ \mu\text{m}$  in N-methylpyrrolidone was applied to a side of each electrode on a screen printing machine using a 400 mesh screen and dried. An adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 10 wt% of alumina powder having an average particle size of  $0.01\ \mu\text{m}$  in N-methylpyrrolidone was applied to the previously coated side of the negative electrode on a screen printing machine using a 200 mesh screen. The previously coated side of the positive electrode was stuck thereto, and the laminate was dried.

#### EXAMPLE 25

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1 except for the following. An adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 50 wt% of carbon powder having an average particle size of  $1\ \mu\text{m}$  (produced by Osaka Gas Co., Ltd.) in N-methylpyrrolidone was applied to a side of each electrode on a screen printing machine using a 400 mesh screen and dried. An adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 10 wt% of alumina powder having an average particle size of  $0.01\ \mu\text{m}$  in N-methylpyrrolidone was applied to the previously coated side of the negative electrode on a screen printing machine using a 200 mesh screen, and the previously coated side of the positive electrode was stuck thereto, followed by drying.

#### EXAMPLE 26

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1 except for the following. An adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 20 wt% of iron powder having an average particle size of 1  $\mu\text{m}$  in N-methylpyrrolidone was applied to a side of each electrode on a screen printing machine using a 400 mesh screen and dried. An adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 30 wt% of silicon carbide powder having an average particle size of 0.5  $\mu\text{m}$  in N-methylpyrrolidone was applied to the previously coated side of the negative electrode on a screen printing machine using a 200 mesh screen. The previously coated side of the positive electrode was stuck thereto, and the resulting laminate was dried. Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1 except for using an adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride, 9 wt% of alumina powder having an average particle size of 0.01  $\mu\text{m}$ , and 1 wt% of iron powder having an average particle size of 0.5  $\mu\text{m}$  in N-methylpyrrolidone.

#### EXAMPLE 27

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1 except for the following. An adhesive resin solution prepared by dissolving

and dispersing 10 wt% of polyvinylidene fluoride and 50 wt% of carbon powder having an average particle size of 1  $\mu\text{m}$  in N-methylpyrrolidone was applied to a side of each electrode on a screen printing machine using a 400 mesh screen and dried. An adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 30 wt% of silicon carbide powder having an average particle size of 0.5  $\mu\text{m}$  in N-methylpyrrolidone was applied to the previously coated side of the negative electrode on a screen printing machine using a 200 mesh screen. The previously coated side of the positive electrode was stuck thereto, and the resulting laminate was dried.

#### EXAMPLE 28

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1 except for the following. An adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 20 wt% of iron powder having an average particle size of 1  $\mu\text{m}$  in N-methylpyrrolidone was applied to a side of each electrode on a screen printing machine using a 400 mesh screen and dried. An adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 5 wt% of polymethyl methacrylate powder having an average particle size of 0.5  $\mu\text{m}$  in N-methylpyrrolidone was applied to the previously coated side of the negative electrode on a screen printing machine using a 200 mesh screen. The previously coated side of the positive electrode

was stuck thereto, and the resulting laminate was dried.

#### EXAMPLE 29

Electrodes were prepared, a battery was assembled, and evaluation was made in the same manner as in Example 1 except for the following. An adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 50 wt% of carbon powder having an average particle size of 1  $\mu\text{m}$  in N-methylpyrrolidone was applied to a side of each electrode on a screen printing machine using a 400 mesh screen and dried. An adhesive resin solution prepared by dissolving and dispersing 10 wt% of polyvinylidene fluoride and 5 wt% of polymethyl methacrylate powder having an average particle size of 0.5  $\mu\text{m}$  in N-methylpyrrolidone was applied to the previously coated side of the negative electrode on a screen printing machine using a 200 mesh screen. The previously coated side of the positive electrode was stuck thereto, and the resulting laminate was dried.

#### EXAMPLE 30

A positive electrode, a negative electrode, and an adhesive resin solution were prepared in the same manner as in Example 1. The positive electrode and the negative electrode were cut in pieces of 50 mm x 50 mm and 55 mm x 55 mm, respectively.

The adhesive resin solution was applied to a side of a cut piece of the negative electrode on a screen printing machine, and a cut piece of the positive electrode was stuck thereto. Then, a side of another piece of the negative electrode was coated with the

adhesive resin solution and bonded to the previously bonded positive electrode. These steps were repeated 6 times to build up a laminated battery body. The battery body was dried while applying pressure to obtain a tabular laminated battery body having positive and negative electrodes alternately bonded via an adhesive resin layer. The battery characteristics of the resulting battery body were evaluated in the same manner as in Example 1.

#### EXAMPLE 31

A positive electrode, a negative electrode, and an adhesive resin solution were prepared in the same manner as in Example 1. The positive electrode and the negative electrode were cut in pieces of 50 mm x 50 mm and 55 mm x 55 mm, respectively.

The adhesive resin solution was applied to a side of a cut piece of the positive electrode on a screen printing machine, and a cut piece of the negative electrode was stuck thereto. Then, a side of another piece of the positive electrode was coated with the adhesive resin solution and bonded to the previously bonded negative electrode. These steps were repeated 6 times to build up a laminated battery body. The battery body was dried while applying pressure to obtain a tabular laminated battery body having positive and negative electrodes alternately bonded with an adhesive resin layer. The battery characteristics of the resulting battery body were evaluated in the same manner as in Example 1.



#### EXAMPLE 32

A positive electrode, a negative electrode, and an adhesive resin solution were prepared in the same manner as in Example 1. A band of 300 mm x 50 mm and of 305 mm x 55 mm was cut out of the positive electrode and the negative electrode, respectively. The adhesive resin solution was applied to a side of the negative electrode band on a screen printing machine. One end of the coated negative electrode was folded back at a prescribed length. The positive electrode band was inserted into the center of the fold, and the folded end was sent to a laminator. Subsequently, the positive electrode and the negative electrode were superposed and passed through the laminator. The laminate was rolled up into an oblong cylinder while applying the adhesive resin solution to the other side of the negative electrode that was opposite to the side previously coated with the adhesive resin solution.

The rolled oblong battery body was dried while applying pressure to obtain a tabular roll type battery body having positive and negative electrodes bonded alternately via an adhesive resin layer. The battery characteristics of the resulting battery body were evaluated in the same manner as in Example 1.

#### EXAMPLE 33

A positive electrode, a negative electrode, and an adhesive resin solution were prepared in the same manner as in Example 1. A band of 300 mm x 50 mm and of 305 mm x 55 mm was cut

out of the positive electrode and the negative electrode, respectively. The adhesive resin solution was applied to a side of the separator on a screen printing machine. One end of the coated positive electrode was folded back at a prescribed length.

The negative electrode band was inserted into the center of the fold. Subsequently, the folded positive electrode and the negative electrode were superposed and passed through the laminator. The adhesive resin solution was applied to the other side of the positive electrode that was opposite to the side previously coated with the adhesive resin solution, and the laminate was rolled up into an oblong cylinder.

The rolled oblong battery body was dried while applying pressure to obtain a tabular roll type battery body having positive and negative electrodes bonded alternately via an adhesive resin layer. The battery characteristics of the resulting battery body were evaluated in the same manner as in Example 1.

#### EXAMPLE 34

A positive electrode, a negative electrode, and an adhesive resin solution were prepared in the same manner as in Example 1. A piece of 50 mm x 50 mm and of 55 mm x 55 mm was cut out of the positive electrode and the negative electrode, respectively. The adhesive resin solution was applied to a side of the negative electrode by means of a roll coater the nip of which was adjusted to give a coating thickness substantially equal to that in Example 1. The negative electrode and the positive

electrode were joined and dried in a drier at 80°C for 1 hour to obtain a battery body comprising a unit electrode body having the positive electrode and the negative electrode bonded together.

The battery characteristics of the resulting battery body were evaluated in the same manner as in Example 1.

#### EXAMPLE 35

A positive electrode, a negative electrode, and an adhesive resin solution were prepared in the same manner as in Example 1. A piece of 50 mm x 50 mm and of 55 mm x 55 mm was cut out of the positive electrode and the negative electrode, respectively. The adhesive resin solution was applied to a side of the negative electrode by means of a gravure printing machine the nip of which was adjusted to give a coating thickness substantially equal to that in Example 1. The negative electrode and the positive electrode were joined and dried in a drier at 80°C for 1 hour to obtain a battery body comprising a unit electrode body having the positive electrode and the negative electrode bonded together. The battery characteristics of the resulting battery body were evaluated in the same manner as in Example 1.

#### EXAMPLE 36

A positive electrode, a negative electrode, and an adhesive resin solution were prepared in the same manner as in Example 1. A piece of 50 mm x 50 mm and of 55 mm x 55 mm was cut out of the positive electrode and the negative electrode, respectively. The adhesive resin solution was applied to a side

of the negative electrode by means of a doctor blade coater the gap of which was adjusted to give a coating thickness substantially equal to that in Example 1. The negative electrode and the positive electrode were joined and dried in a drier at 80°C for 1 hour to obtain a battery body comprising a unit electrode body having the positive electrode and the negative electrode bonded together.

The battery characteristics of the resulting battery body were evaluated in the same manner as in Example 1.

#### EXAMPLE 37

A positive electrode, a negative electrode, and an adhesive resin solution were prepared in the same manner as in Example 1. A piece of 50 mm x 50 mm and of 55 mm x 55 mm was cut out of the positive electrode and the negative electrode, respectively. The adhesive resin solution was applied to a side of the negative electrode by means of a bar coater the gap of which was adjusted to give a coating thickness substantially equal to that in Example 1. The negative electrode and the positive electrode were joined and dried in a drier at 80°C for 1 hour to obtain a battery body comprising a unit electrode body having the positive electrode and the negative electrode bonded together.

The battery characteristics of the resulting battery body were evaluated in the same manner as in Example 1.

The adhesive strength of the prepared electrodes and the discharge capacity in charging and discharging the prepared batteries at 1C are shown in Tables 1 through 9. The graphs of

discharge capacity vs. charging and discharging current with different adhesive resins are shown in Figs. 3 and 4. Comparisons between Example 1 and Comparative Example 1 and between Example 2 and Comparative Example 2 reveal that addition of a filler to an adhesive resin solution brings about improvement in discharge capacity, especially under a high load.

TABLE 1

	Adhesive				Peel Strength (gf/cm)	Discharge Capacity (1C) (mAh)
	Resin	Filler	Weight Ratio	Particle Size of Filler		
Example 1	PVDF	alumina	1:1	0.01	50	60
Compara. Example 1	PVDF	none	-	-	100	20
Example 2	PVA	alumina	2:5	0.01	70	60
Compara. Example 2	PVA	none	-	-	100	30

Table 2 shows the results obtained with the average particle size of an alumina filler varied and the results obtained with a silica filler having a smaller particle size. These results are graphed in Fig. 5, in which the peel strength and the discharge capacity are plotted against the particle size of the alumina filler added. It can be seen that the peel strength somewhat decreases at a particle size of 1  $\mu\text{m}$  or smaller, which was not problematical for practical use. It is also seen that, on the other hand, the discharge capacity tends to decrease as the average particle size

becomes greater than 1  $\mu\text{m}$  because of reduction of void volume in the adhesive resin layer.

TABLE 2

	Adhesive				Peel Strength (gf/cm)	Discharge Capacity (1C) (mAh)
	Resin	Filler	Weight Ratio	Particle Size of Filler		
Example 1	PVDF	alumina	1:1	0.01	50	60
Example 3	PVDF	alumina	1:1	0.1	60	55
Example 4	PVDF	alumina	1:1	1	65	50
Example 5	PVDF	silica	1:1	0.007	45	60
Compara. Example 3	PVDF	alumina	1:1	10	60	25

Table 3 shows the results obtained when the ratio of the alumina filler to the adhesive resin was varied. These results are graphed in Fig. 6, in which the peel strength and the battery capacity are plotted against volume percentage of the voids. The proportion of the adhesive resin in the void volume formed by the filler changes with a change of the filler to resin ratio, and a change of the void volume in the adhesive resin layer follows. If the volume percentage of the voids is 20% or less, passages for ions through the adhesive resin layer are diminished, resulting in an obvious reduction in discharge capacity. On the other hand, the adhesive strength tends to reduce with an increase of volume percentage of the voids. If the volume percentage of the voids is 80% or more, the amount of the filler is so large that the amount

of the adhesive resin is insufficient, resulting in an extreme reduction in adhesive strength.

Table 4 shows the results obtained when the thickness of the adhesive resin layer was varied. The peel strength and the discharge capacity are plotted against the thickness in Fig. 7.

As can be seen, with a coating thickness of 50  $\mu\text{m}$  or smaller, the adhesive resin layer does not cause hindrance to ion conduction while filling the gap formed by the unevenness of the electrodes so that a high discharge capacity can be secured. If the thickness exceeds 50  $\mu\text{m}$ , the passages for ions are so long that they become resistance and cause gradual reduction of discharge capacity. If the thickness of the adhesive resin layer is increased to about 200  $\mu\text{m}$ , the rate of reduction in discharge capacity is as high as about 50%.

TABLE 3

	Adhesive				Volume of Solid Matter (%)	Void Volume (%)	Peel Strength (gf/cm)	Discharge Capacity (1C) (mAh)
	Resin	Filler	Weight Ratio	Particle Size of Filler				
Example 1	PVDF	alumina	1:1	0.01	50	50	70	62
Example 6	PVDF	alumina	2:1	0.01	70	30	85	58
Example 7	PVDF	alumina	1:5	0.01	30	70	60	65
Compara. Example 4	PVDF	alumina	10:1	0.01	90	10	100	20
Compara. Example 5	PVDF	alumina	1:10	0.01	10	90	20	65



TABLE 4

	Adhesive				Thick- ness ( $\mu\text{m}$ )	Peel Strength (gf/cm)	Discharge Capacity (1C) (mAh)
	Resin	Filler	Weight Ratio	Particle Size of Filler			
Example 1	PVDF	alumina	1:1	0.01	20	70	60
Example 8	PVDF	alumina	1:1	0.01	50	70	58
Example 9	PVDF	alumina	1:1	0.01	100	70	55
Example 10	PVDF	alumina	1:1	0.01	150	70	50
Example 11	PVDF	alumina	1:1	0.01	10	60	60
Example 12	PVDF	alumina	1:1	0.01	200	70	30

Fig. 5 shows the results obtained from different kinds of fillers. It was proved that various fillers produce similar effects. In particular, great effects are obtained with inorganic compounds and polymers.

TABLE 5

	Adhesive				Peel Strength (gf/cm)	Discharge Capacity (1C) (mAh)
	Resin	Filler	Weight Ratio	Particle Size of Filler		
Example 1	PVDF	alumina	1:1	0.01	50	60
Example 13	PVDF	silica	1:1	0.01	50	60
Example 14	PVDF	silicon carbide	1:3	0.5	80	50
Example 15	PVDF	boron carbide	1:3	0.5	80	50
Example 16	PVDF	silicon nitride	1:3	0.5	80	50
Example 17	PVDF	PMMA	2:1	0.5	80	50

Table 6 shows the results obtained when two kinds of fillers were used in combination. It is seen that similar effects are produced when fillers are used in various combinations. It is understood, in particular, that materials that contain no conducive materials show great effects.

TABLE 6

	Adhesive								Peel Strength	Discharge Capacity (1C) (mAh)
	Resin			Filler 1			Filler 2			
Kind	Weight Ratio	Kind	Weight Ratio	Average Particle Size	Kind	Weight Ratio	Average Particle Size			
Example 1	PVDF	1	alumina	1	0.01	none	0	0	50	60
Example 18	PVDF	1	alumina	0.9	0.01	alumina	0.1	1	55	55
Example 19	PVDF	1	alumina	0.9	0.01	silica	0.5	0.01	50	60
Example 20	PVDF	1	alumina	0.9	0.01	silica	0.1	0.5	55	55
Example 21	PVDF	1	alumina	0.9	0.01	PMMA	0.1	0.5	55	55
Example 22	PVDF	1	alumina	0.9	0.01	silicon carbide	0.1	0.5	55	55
Example 23	PVDF	1	silicon carbide	0.5	0.5	PMMA	0.5	0.5	80	55

Table 7 shows the results obtained in case where the adhesive resin layer provided had a three layer structure having an insulating filler-containing adhesive resin layer (intermediate layer) between conductive filler-containing adhesive resin layers (electrode surface layers). It is understood that similar effects are obtained from various combinations of a conductive filler and an insulating filler.

TABLE 7

	Adhesive													Peel Strength (gf/cm)	Dis-charge Capa-city (1C) (mAh)
	Adhesive Resin Layer (Intermediate Layer)						Adhesive Resin Layer (Electrode Surface Layer)								
	Adhesive Resin			Filler			Adhesive Resin				Filler				
	Kind	Weight Ratio	Kind	Weight Ratio	Average Size	Kind	Weight Ratio	Kind	Weight Ratio	Kind	Weight Ratio	Average Size			
Example 1	PVDF	1	alumina	1	0.01	none	-	-	1	-	-	50	60		
Example 24	PVDF	1	alumina	1	0.01	PVDF	1	iron	1	0.5	55	50			
Example 25	PVDF	1	alumina	1	0.01	PVDF	1	carbon	1	1	55	50			
Example 26	PVDF	1	silicon carbide	1	0.5	PVDF	1	iron	1	0.5	80	45			
Example 27	PVDF	1	silicon carbide	1	0.5	PVDF	1	carbon	1	1	80	45			
Example 28	PVDF	1	PMMA	1	0.5	PVDF	1	iron	1	0.5	80	45			
Example 29	PVDF	1	PMMA	1	0.5	PVDF	1	carbon	1	1	80	45			

Table 8 shows the results of testing on battery characteristics of various battery structures. It proves that satisfactory battery characteristics can be obtained irrespective of the battery structure.

TABLE 8

	Adhesive				Battery Structure	Discharge Capacity (1C) (mAh)
	Resin	Filler	Weight Ratio	Particle Size of Filler		
Example 1	PVDF	alumina	1:1	0.01	tabular unit electrode body	60
Example 30	PVDF	alumina	1:1	0.01	tabular laminated electrode body	360
Example 31	PVDF	alumina	1:1	0.01	"	360
Example 32	PVDF	alumina	1:1	0.01	tabular rolled electrode body	360
Example 33	PVDF	alumina	1:1	0.01	"	360

Table 9 shows the results of testing on battery characteristics obtained when the method for applying the adhesive resin solution was altered. As shown in Table 9, satisfactory battery characteristics can be obtained irrespective of the application method as long as the coating thickness is substantially equal.

TABLE 9

	Adhesive				Method of Adhesive Application	Discharge Capacity (1C) (mAh)
	Resin	Filler	Weight Ratio	Particle Size of Filler		
Example 1	PVDF	alumina	1:1	0.01	screen printing	60
Example 34	PVDF	alumina	1:1	0.01	roll coater	60
Example 35	PVDF	alumina	1:1	0.01	gravure printing	60
Example 36	PVDF	alumina	1:1	0.01	doctor blade	60
Example 37	PVDF	alumina	1;1	0.01	bar coater	60

#### Industrial Applicability

The battery according to the invention is used as a secondary battery, etc. in portable electronic equipment and has reduced size and weight as well as improved battery performance.

## CLAIMS

1. A battery comprising a battery body including:  
a positive and a negative electrode containing an active material,  
an electrolytic solution containing an electrolyte, and  
an adhesive resin layer which is interposed in between the positive electrode and the negative electrode and is joined to at least one of the positive and the negative electrodes,  
wherein the adhesive resin layer comprises at least one layer and contains fillers.
2. A battery according to claim 1, wherein said electrolyte is an organic electrolyte containing lithium ions.
3. A battery according to claim 1, wherein the average particle size of said filler is equal to or smaller than the particle size of the active material constituting each electrode.
4. A battery according to claim 1, wherein said average particle size of said filler is 1  $\mu\text{m}$  or smaller.
5. A battery according to claim 1, wherein the sum of a volume ratio of the adhesive resin and that of the filler per unit volume of said adhesive resin layer is less than 1.



6. A battery according to claim 1, wherein the sum of a volume ratio of the adhesive resin and that of the filler per unit volume of said adhesive resin layer is 0.2 to 0.8.

7. A battery according to claim 1, wherein said filler comprises at least one of non-conductive materials and semiconductors.

8. A battery according to claim 1, wherein said adhesive resin layer comprises a layer containing an electrically conductive filler and a layer containing at least one of non-conductive fillers and semiconductive fillers.

9. A battery according to claim 1, wherein said adhesive resin layer is constituted so as to fill the unevenness of the positive electrode and the negative electrode.

10. A battery according to claim 1, wherein said battery body is a laminate of a plurality of electrode bodies each composed of a single layer of the positive electrode, a single layer of the adhesive resin layer, and a single layer of the negative electrode.

11. A battery according to claim 10, wherein said laminate is composed of the positive electrodes and the negative

electrodes interposed alternately among a plurality of the adhesive resin layers.

12. A battery according to claim 10, wherein said laminate is composed of the positive electrode and the negative electrode which are alternately interposed between adhesive resin layers and rolled up.

13. A battery according to claim 10, wherein said laminate is composed of the positive electrode and the negative electrode which are alternately interposed between adhesive resin layers and folded.

## ABSTRACT

Conventional batteries are disadvantageous in that a firm outer case must be used to maintain an electrical connection between electrodes, which has been an obstacle to size reduction. Those in which each electrode and a separator are joined with an adhesive resin suffer from conflict between adhesive strength and battery characteristics, particularly ion conductivity and internal resistivity. To solve these problems, it is an object of the invention to reduce resistance between electrodes, i.e., internal resistance of a battery to improve battery characteristics while securing both insulation function against electron conduction and ion conductivity between electrodes and also to maintain adhesive strength enough to firmly join the electrodes thereby to provide a light, compact and thin battery.

The internal resistivity can be diminished by joining a positive electrode and a negative electrode with an adhesive resin layer having at least one adhesive resin layer containing a filler.

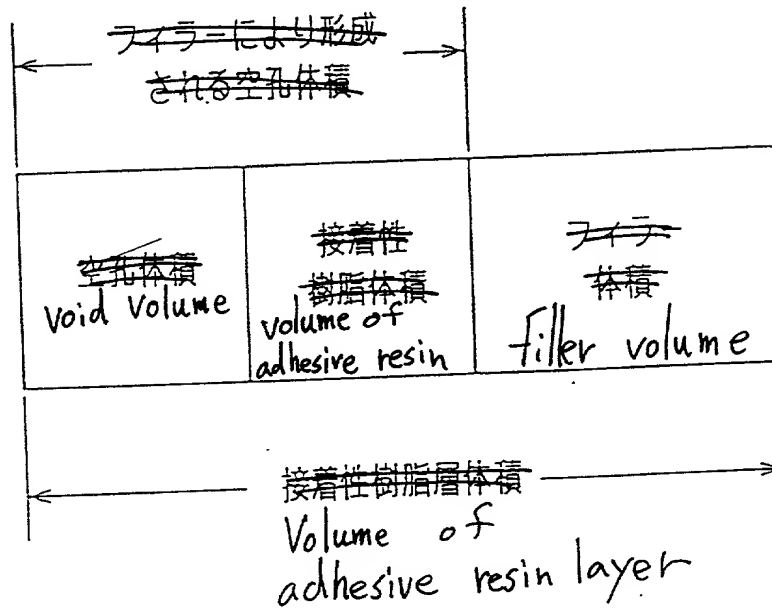
The adhesive resin layer has pores, which are filled with an electrolytic solution to exhibit sufficient ion conductivity thereby to improve battery characteristics and to retain adhesive strength.

1/7

FIG. 1

~~第 1 図~~

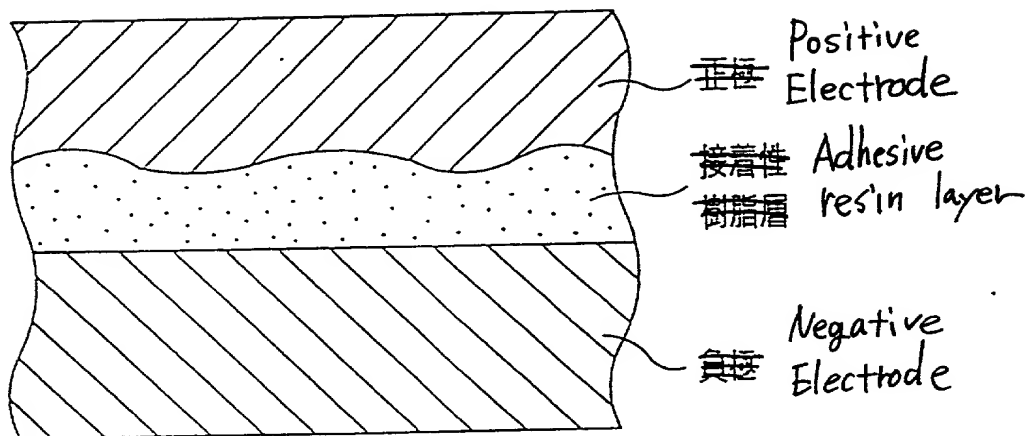
Void volume formed by filler.



0051-2521-0 SHEET 1 OF 7

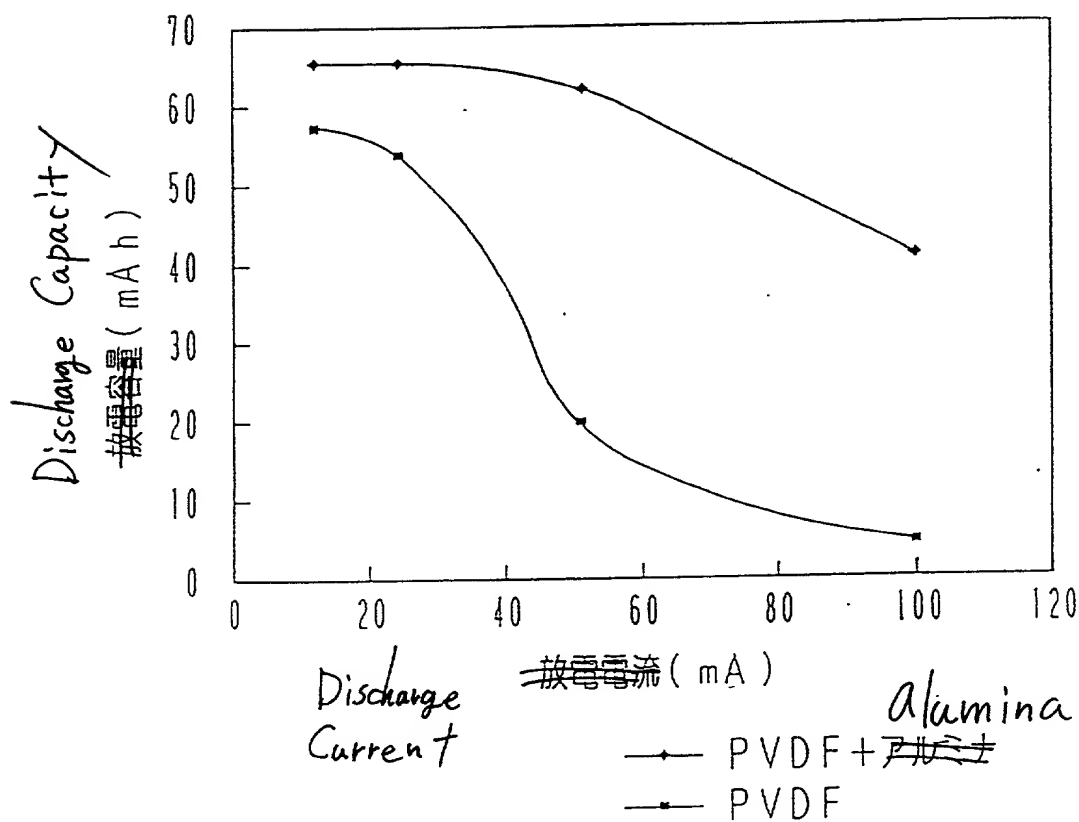
2/7

FIG. 2

~~第 2 圖~~

3/7

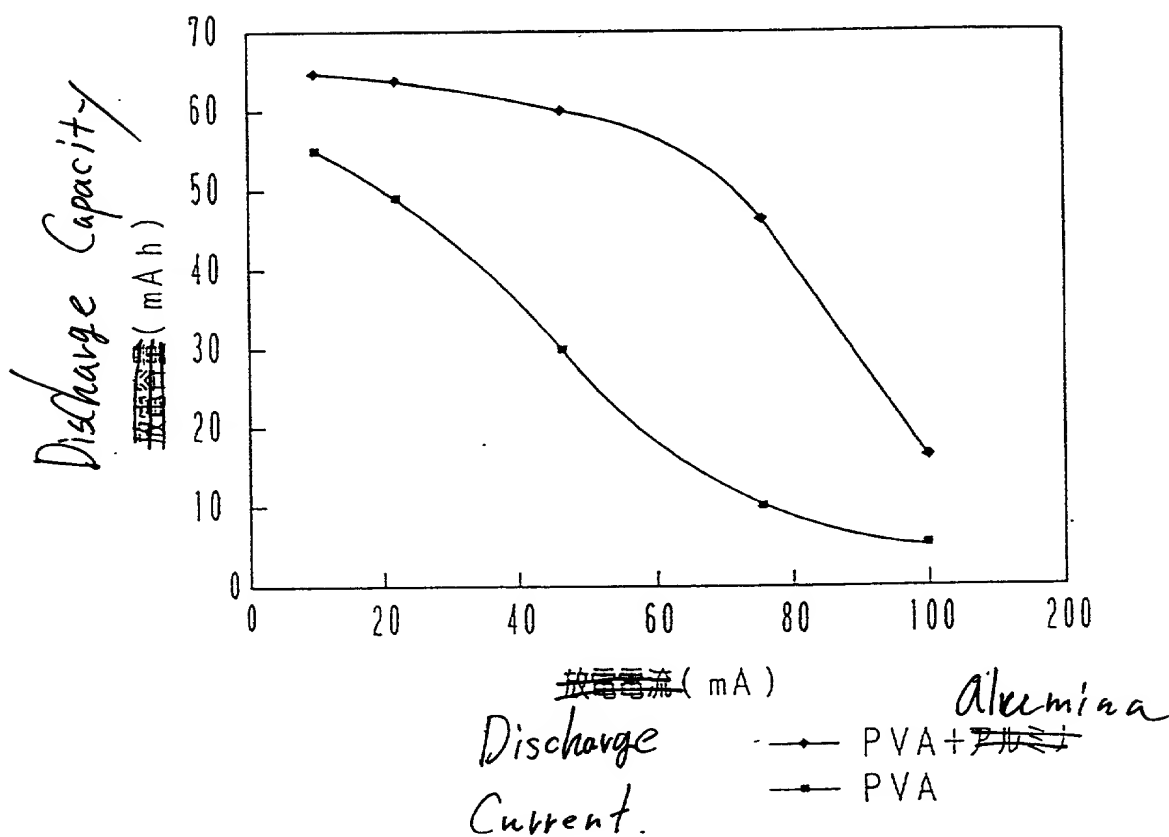
FIG. 3

~~第 3 圖~~

4/7

FIG. 4

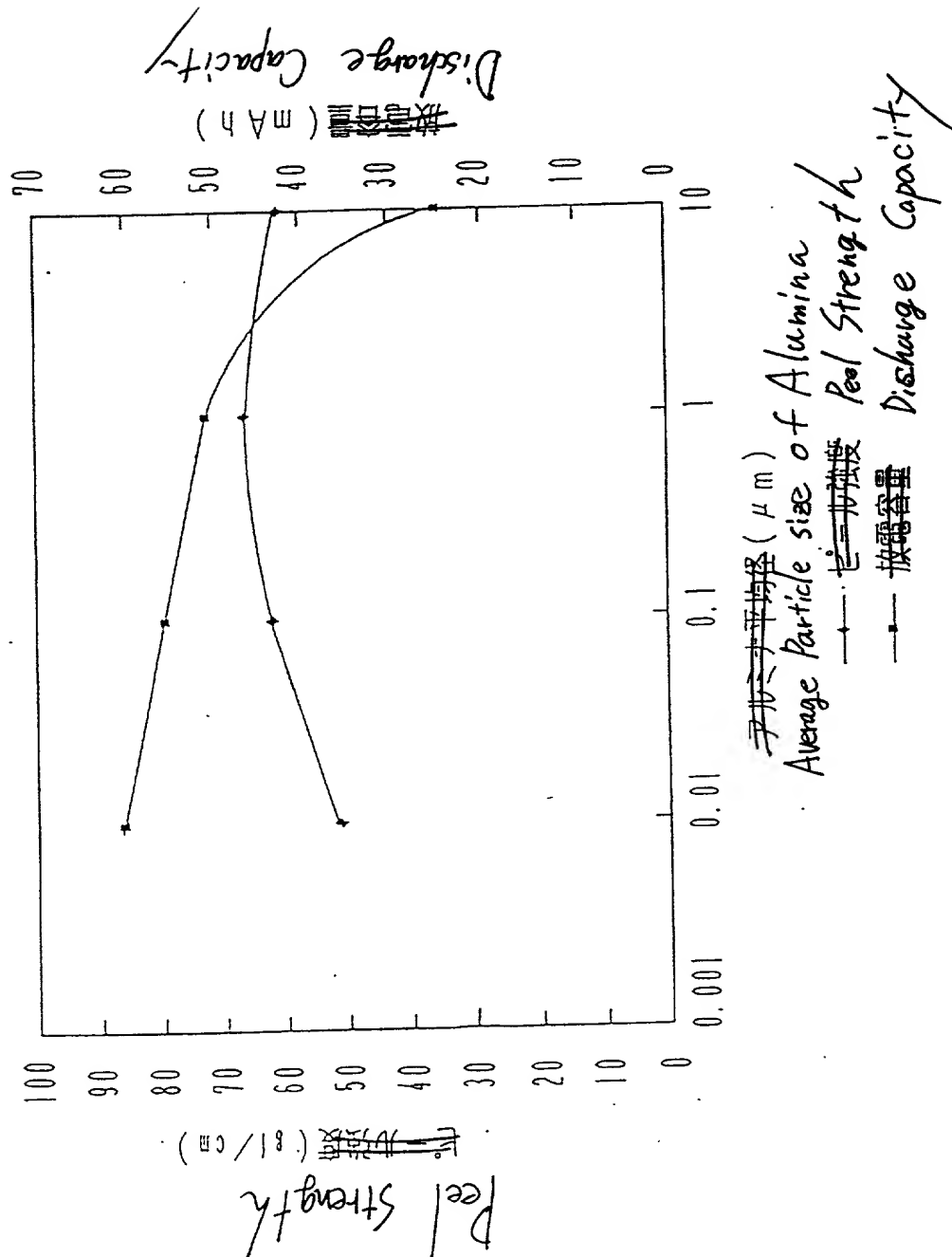
~~第 4 圖~~



5/7

FIG. 5

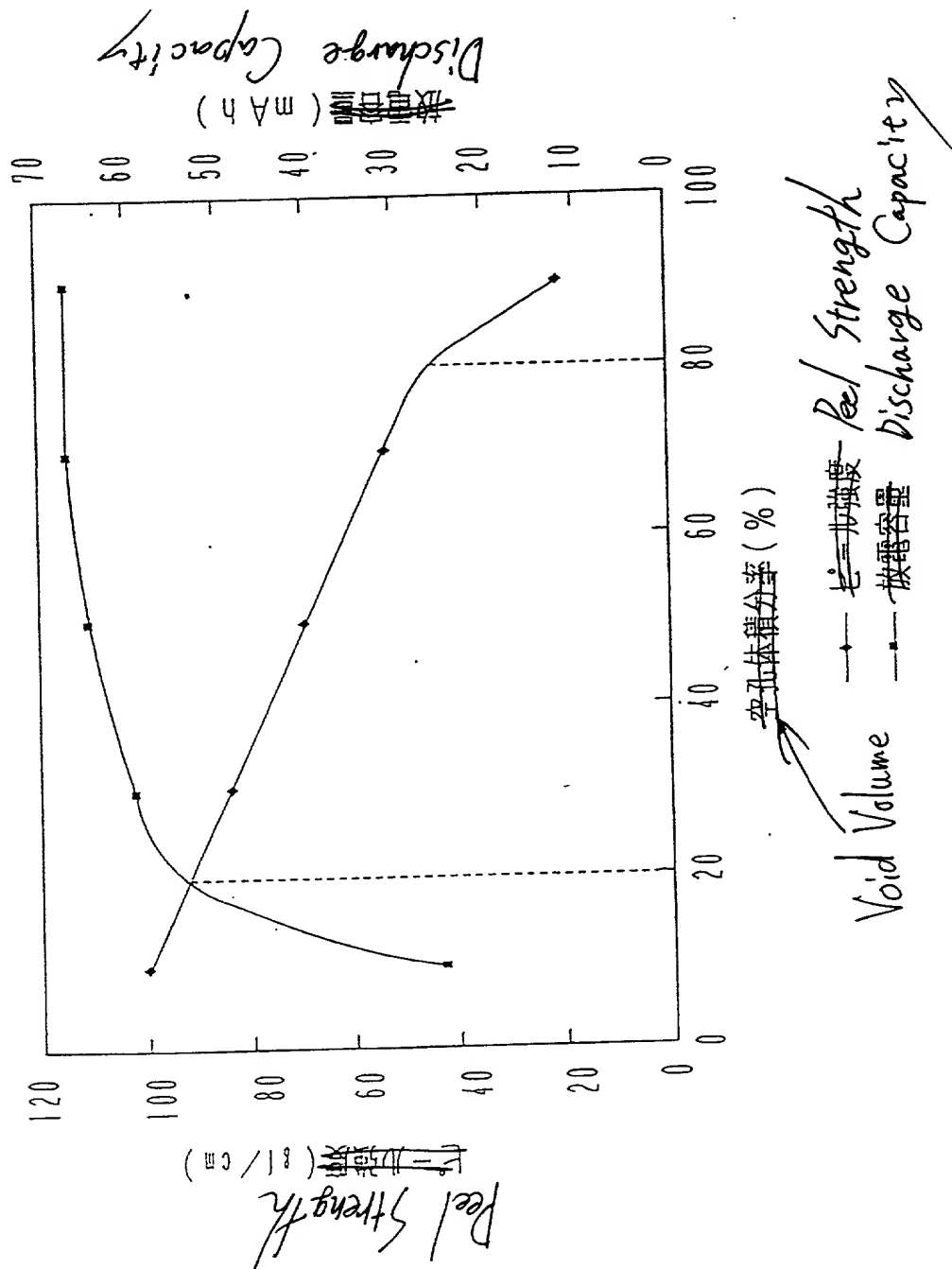
~~第 5 图~~





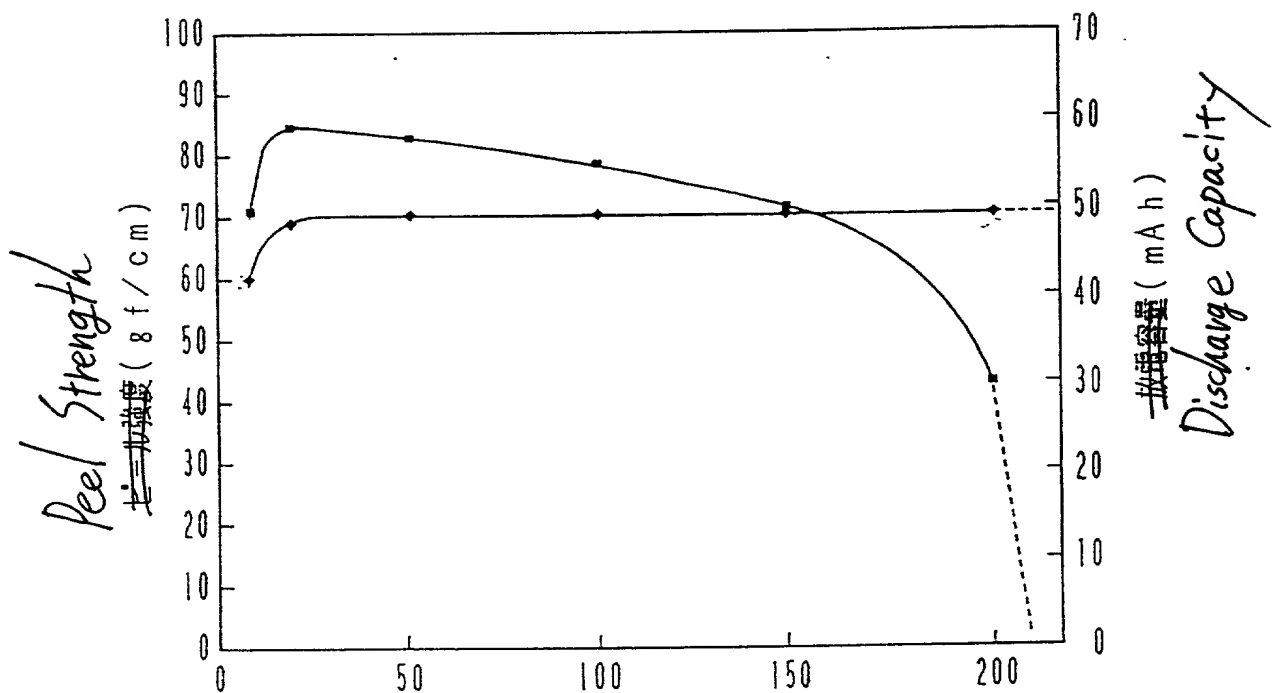
6/7

FIG. 6  
~~第 6 圖~~



7/7

FIG. 7

~~第 7 図~~~~接着性樹脂層厚み ( $\mu\text{m}$ )~~

Thickness of Adhesive resin layer

$\bullet$  ~~ピール強度~~ Peel Strength  
 $\blacksquare$  ~~放電容量~~ Discharge Capacity

# Declaration and Power of Attorney For Patent Application

## 特許出願宣言書及び委任状

### Japanese Language Declaration

#### 日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

As a below named inventor, I hereby declare that:

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

My residence, post office address and citizenship are as stated next to my name.

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者（下記の名称が複数の場合）であると信じています。

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled.

BATTERY

上記発明の明細書は、

the specification of which

☐ 本書に添付されています。

☐ is attached hereto.

☐ 月 日 に提出され、米国出願番号または特許協定条約国際出願番号を \_\_\_\_\_ とし、  
(該当する場合) \_\_\_\_\_ に訂正されました。

☒ was filed on January 22, 1999  
as United States Application Number or  
PCT International Application Number  
PCT/JP98/00248 and was amended on  
\_\_\_\_\_ (if applicable).

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

私は、連邦規則法典第37編第1条56項に定義されるとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

Japanese Language Declaration  
(日本語宣言書)

私は、米国法典第35編119条 (a) - (d) 項又は365条 (b) 項に基づき下記の、米国以外の国の少なくとも一カ国を指定している特許協力条約365 (a) 項に基づく国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している、本出願の前に出願された特許または発明者証の外国出願を以下に、枠内をマークすることで、示しています。

Prior Foreign Application(s)  
外国での先行出願

(Number) (番号)	(Country) (国名)
(Number) (番号)	(Country) (国名)

I hereby claim foreign priority under Title 35, United States Code, Section 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

	Priority Claimed 優先権主張
(Day/Month/Year Filed) (出願年月日)	<input type="checkbox"/> Yes はい <input type="checkbox"/> No いいえ
(Day/Month/Year Filed) (出願年月日)	<input type="checkbox"/> Yes はい <input type="checkbox"/> No いいえ

私は、第35編米国法典119条 (e) 項に基づいて下記の米国特許出願規定に記載された権利をここに主張いたします。

(Application No.) (出願番号)	(Filing Date) (出願日)
-----------------------------	------------------------

私は、下記の米国法典第35編120条に基づいて下記の米国特許出願に記載された権利、又は米国を指定している特許協力条約365条 (c) に基づく権利をここに主張します。また、本出願の各請求範囲の内容が米国法典第35編112条第1項又は特許協力条約で規定された方法で先行する米国特許出願に開示されていない限り、その先行米国出願書提出日以降で本出願書の日本国内または特許協力条約国際提出日までの期間中に入手された、連邦規則法典第37編1条56項で定義された特許資格の有無に関する重要な情報について開示義務があることを認識しています。

(Application No.) (出願番号)	(Filing Date) (出願日)
-----------------------------	------------------------

(Application No.) (出願番号)	(Filing Date) (出願日)
-----------------------------	------------------------

私は、私自信の知識に基づいて本宣言書中で私が行なう表明が真実であり、かつ私の入手した情報と私の信じることに基づく表明が全て真実であると信じていること、さらに故意になされた虚偽の表明及びそれと同等の行為は米国法典第18編第1001条に基づき、罰金または拘禁、もしくはその両方により処罰されること、そしてそのような故意による虚偽の声明を行なえば、出願した、又は既に許可された特許の有効性が失われることを認識し、よってここに上記のごとく宣誓を致します。

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

(Application No.) (出願番号)	(Filing Date) (出願日)
-----------------------------	------------------------

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code Section 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of application.

(Status: Patented, Pending, Abandoned) (現況：特許許可済、係属中、放棄済)
--

(Status: Patented, Pending, Abandoned) (現況：特許許可済、係属中、放棄済)
--

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of the application or any patent issued thereon.

## Japanese Language Declaration

(日本語宣言書)

委任状：私は下記の発明者として、本出願に関する一切の手続きを米特許商標局に対して遂行する弁理士または代理人として、下記の者を指名いたします。

(弁護士、または代理人の指名及び登録番号を明記のこと)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: (list name and registration number)

Norman F. Oblon, Reg. No. 24,618; Marvin J. Spivak, Reg. No. 24,913; C. Irvin McClelland, Reg. No. 21,124; Gregory J. Maier, Reg. No. 25,599; Arthur I. Neustadt, Reg. No. 24,854; Richard D. Kelly, Reg. No. 27,757; James D. Hamilton, Reg. No. 28,421; Eckhard H. Kuesters, Reg. No. 28,870; Robert T. Pous, Reg. No. 29,099; Charles L. Gholz, Reg. No. 26,395; Vincent J. Sunderdick, Reg. No. 29,004; William E. Beaumont, Reg. No. 30,996; Steven B. Kelber, Reg. No. 30,073; Robert F. Gruse, Reg. No. 27,295; Jean-Paul Lavalle, Reg. No. 31,451; Stephen G. Baxter, Reg. No. 32,884; Martin M. Zoltick, Reg. No. 35,745; Robert W. Hahl, Reg. No. 33,893; Richard L. Treanor, Reg. No. 36,379; Steven P. Weihrouh, Reg. No. 32,829; John T. Goolkasian, Reg. No. 26,142; Marc R. Labgold, Reg. No. 34,651; William J. Healey, Reg. No. 36,160; Richard L. Chinn, Reg. No. 34,305; Steven E. Lipman, Reg. No. 30,011; Carl E. Schlier, Reg. No. 34,426; James J. Kulbaski, Reg. No. 34,648; Catherine B. Richardson, Reg. No. 39,007; Richard A. Neifeld, Reg. No. 35,299; J. Derek Mason, Reg. No. 35,270; and Surinder Sachar, Reg. No. 34,423, with full powers of substitution and revocation.

書類送付先

Send Correspondence to:

OBLON, SPIVAK, MCCLELLAND, MAIER & NEUSTADT, P.C.  
FOURTH FLOOR  
1755 JEFFERSON DAVIS HIGHWAY  
ARLINGTON, VIRGINIA 22202 U.S.A.

直接電話連絡先：(名前及び電話番号)

Direct Telephone Calls to: (name and telephone number)

(703) 413-3000

単独発明者または第一の共同発明者の氏名	Full name of sole or first joint inventor
発明者の署名	Inventor's signature
住所	Residence
国籍	Citizenship
郵便の宛先	Post Office Address
第二の共同発明者の氏名	Full name of second joint inventor, if any
第二の共同発明者の署名	Second joint Inventor's signature
住所	Residence
国籍	Citizenship
郵便の宛先	Post Office Address

Handwritten notes: 1st inventor: Shigeru AIHARA, Date: August 25, 1999, Residence: Tokyo, Japan, Citizenship: Japan, Post Office Address: c/o Mitsubishi Denki Kabushiki Kaisha, 2-3, Marunouchi 2-chome, Chiyoda-ku, Tokyo 100 Japan. 2nd inventor: Daigo TAKEMURA, Date: August 25, 1999, Residence: Tokyo, Japan, Citizenship: Japan, Post Office Address: c/o Mitsubishi Denki Kabushiki Kaisha, 2-3, Marunouchi 2-chome, Chiyoda-ku, Tokyo 100 Japan.

(第三以降の共同発明者についても同様に記載し、署名すること)

(Supply similar information and signature for third and subsequent joint inventors.)

Japanese Language Declaration  
(日本語宣言書)

第三共同発明者名 (該当する場合)		Full name of third joint inventor, if any	
		<u>3rd</u> Hisashi SHIOTA	
第三発明者の署名	日付	Third inventor's signature	Date
		<u>Hisashi Shiota</u>	August 25, 1999
住所		Residence	
		Tokyo, Japan <u>Spt</u>	
国籍		Citizenship	
		Japan	
郵便の宛先		Post office address	
		c/o Mitsubishi Denki Kabushiki Kaisha,	
		2-3, Marunouchi 2-chome, Chiyoda-ku,	
		Tokyo 100 Japan	
第四共同発明者名 (該当する場合)		Full name of fourth joint inventor, if any	
		<u>4th</u> Jun ARAGANE	
第四発明者の署名	日付	Fourth inventor's signature	Date
		<u>Jun Aragane</u>	August 25, 1999
住所		Residence	
		Tokyo, Japan <u>Spt</u>	
国籍		Citizenship	
		Japan	
郵便の宛先		Post office address	
		c/o Mitsubishi Denki Kabushiki Kaisha,	
		2-3, Marunouchi 2-chome, Chiyoda-ku,	
		Tokyo 100 Japan	
第五共同発明者名 (該当する場合)		Full name of fifth joint inventor, if any	
		<u>5th</u> Hiroaki URUSHIBATA	
第五発明者の署名	日付	Fifth inventor's signature	Date
		<u>Hiroaki Urushibata</u>	August 25, 1999
住所		Residence	
		Tokyo, Japan <u>Spt</u>	
国籍		Citizenship	
		Japan	
郵便の宛先		Post office address	
		c/o Mitsubishi Denki Kabushiki Kaisha,	
		2-3, Marunouchi 2-chome, Chiyoda-ku,	
		Tokyo 100 Japan	
第六共同発明者名 (該当する場合)		Full name of sixth joint inventor, if any	
		<u>6th</u> Yasuhiro YOSHIDA	
第六発明者の署名	日付	Sixth inventor's signature	Date
		<u>Yasuhiro Yoshida</u>	August 25, 1999
住所		Residence	
		Tokyo, Japan <u>Spt</u>	
国籍		Citizenship	
		Japan	
郵便の宛先		Post office address	
		c/o Mitsubishi Denki Kabushiki Kaisha,	
		2-3, Marunouchi 2-chome, Chiyoda-ku,	
		Tokyo 100 Japan	

# Japanese Language Declaration (日本語宣言書)

第七共同発明者名 (該当する場合)		Full name of seventh joint inventor, if any	
第七発明者の署名	日付	Kouji HAMANO	
		Seventh inventor's signature	Date
		Kouji Hamano	August 25, 1999
住所		Residence	
		Tokyo, Japan Jpt	
国籍		Citizenship	
		Japan	
郵便の宛先		Post office address	
		c/o Mitsubishi Denki Kabushiki Kaisha,	
		2-3, Marunouchi 2-chome, Chiyoda-ku,	
		Tokyo 100 Japan	
第八共同発明者名 (該当する場合)		Full name of eighth joint inventor, if any	
第八発明者の署名	日付	Michio MURAI	
		Eighth inventor's signature	Date
		Michio Murai	August 25, 1999
住所		Residence	
		Tokyo, Japan Jpt	
国籍		Citizenship	
		Japan	
郵便の宛先		Post office address	
		c/o Mitsubishi Denki Kabushiki Kaisha,	
		2-3, Marunouchi 2-chome, Chiyoda-ku,	
		Tokyo 100 Japan	
第九共同発明者名 (該当する場合)		Full name of ninth inventor, if any	
第九発明者の署名	日付	Takayuki INUZUKA	
		Ninth inventor's signature	Date
		Takayuki Inuzuka	August 25, 1999
住所		Residence	
		Tokyo, Japan Jpt	
国籍		Citizenship	
		Japan	
郵便の宛先		Post office address	
		c/o Mitsubishi Denki Kabushiki Kaisha,	
		2-3, Marunouchi 2-chome, Chiyoda-ku,	
		Tokyo 100 Japan	
第十共同発明者名 (該当する場合)		Full name of tenth joint inventor, if any	
第十発明者の署名	日付	Tenth inventor's signature	Date
住所		Residence	
国籍		Citizenship	
郵便の宛先		Post office address	